

## APPENDIX A

# Historical Data Quality and Usability Assessment – Tittabawassee River and Floodplain Remedial Investigation Work Plan

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This appendix documents the quality and usability of historical data for possible use in Remedial Investigation (RI) planning and data evaluation with regard to the nature and extent of potential constituents of interest (PCOIs). The following items are addressed in this appendix:

- Sources of analytical data incorporated into the Midland Offsite Corrective Action (MOCA) database
- Criteria used to assess the quality of the historical data sets and development of data usability classifications for Tittabawassee River and Floodplain RI planning and data evaluation activities
- Outcomes of the categorization process

Tittabawassee River Floodplain Scoping Study data (CH2M HILL, 2005d) are not evaluated in this appendix. A separate data quality evaluation for these data is provided as an attachment to Appendix B of the Tittabawassee River and Floodplain Remedial Investigation Work Plan (RIWP).

## Data Sources

A number of environmental studies and data collection activities have been completed in the Midland, Tittabawassee River, and Saginaw River areas since the 1970s. The purposes of these investigations varied, ranging from general characterization to preliminary assessments of risk posed by human exposure to the chemicals found. The analytical data for a number of these studies and monitoring efforts were incorporated into the analytical database created to support The Dow Chemical Company (Dow) Michigan Operations MOCA program.

Sixteen (16) data sources included results for samples obtained in and along the Tittabawassee River and Floodplain study area. These data sources are listed in Table A-1 (several of these sources also include data for samples collected outside the study area; therefore, all environmental media listed may not include samples collected in the Tittabawassee River and floodplain area).

## Data Quality and Usability Criteria and Categories

Given the varied purposes (or objectives) of the listed investigations, and the time period in which some of the samples were collected, these analytical data may not be of equivalent

quality for data evaluation purposes. A consistent process was employed to assess the overall quality of the historical data sets and to gauge their usability for RI planning and data evaluation. This process consisted of reviewing all readily available documentation from the different investigation sources listed in the MOCA database, assessing its quality, and assigning a data usability category to the analytical data associated with the investigation sources.

Environmental data and reports associated with samples collected in the Tittabawassee River and floodplain area were identified and obtained from various sources including Dow, Dow consultants, Michigan Department of Environmental Quality (MDEQ), Michigan State University (MSU), U.S. Army Corps of Engineers (USACE), and the U.S. Environmental Protection Agency (USEPA). As indicated in Table A-1, certain reports associated with older data could not be located or were incomplete.

Analytical data contained in the reports, work plans, and other documents were then assessed for quality using established USEPA criteria and guidelines for data quality including information from the *Contract Laboratory Program National Functional Guidelines for Inorganic/Organic Data Review* (USEPA, 1999; USEPA, 2001; USEPA, 2004). The assessment considered the quality assurance/quality control (QA/QC) characteristics of the entire analytical data set associated with a data source, and did not include detailed QA/QC screening or validation of individual data points. The primary parameters used to review the quality of the data and establish categories of data usability are listed below.

- **Traceability** – Was chain-of-custody (COC) information available, complete, and attached to the report or supporting documentation package? Absence of COC information was not cause for rejection of the data set. If documentation other than COC was available, professional judgment was used to establish traceability. For example, references to the COC form in the text of a report or other documentation consistent with standard practices were sufficient to document traceability.
- **Comparability** – Were the analytical procedures/methods and detection limits identified and do they represent the accepted industry standards at the time the samples were collected? Data sets greater than 10 years old were downgraded to a less usable category because of possible detection limit issues, and because these older results may not accurately represent current conditions due to possible changes in chemical concentrations over time.
- **Sample Integrity** – Were sample holding times met? Did the sample, as received by the analytical laboratory, meet pertinent and published guidance (for example, temperature criteria, adequate sample volume, appropriate methods of preservation, and so on)?
- Were laboratory QC data available to assess accuracy and precision and were these data within established control limits? Some typical laboratory QC parameters used to assess accuracy and precision include:
  - Initial and continuing calibration
  - Instrument tuning for organic compound (gas chromatography/mass spectroscopy [GC/MS]) measurements

- Internal standards for organic compound measurements
- Interference checks, serial dilutions for metals measurement
- Laboratory blank sample measurements
- Accuracy and precision measurements to include surrogates for organics, laboratory control standards, matrix spikes, matrix spike duplicates, duplicates for metals
- Laboratory-specific method detection levels and associated procedures
- Field QC samples, including blanks and replicates

The data associated with each investigation source was then assigned one of the following categories based on the finding of the review:

- **Category 1 – Data of Known Quality.** These are data that are supported by QA/QC protocols and sampling procedures described in work plans or investigation reports. Data from sources assigned to Category 1 can be used for most RI planning and may be incorporated into RI data evaluation groups, provided that specific analytes, detection limits, and sample locations meet the DQOs for specific end uses.
- **Category 2 – Data of Partially Known Quality.** These data sets have associated with them a limited body of supporting QA/QC information. Although not sufficient to be considered Category 1, the level of quality information is considered suitable for qualitative use in RI planning.
- **Category 3 – Data of Unknown Quality.** These data sets include sample concentration information but lack an adequate level of supporting QA/QC information. These data sets are not considered suitable for quantitative RI uses. However, depending on the reputability of the data sources, these data sets may be used on a limited or provisional basis for qualitative comparisons with other Category 1 and Category 2 data sets.

## Summary of Data Usability Categorization Findings

The findings of the data usability evaluation for each Tittabawassee River area data source are detailed in Table A-1. This table lists the investigating agency, associated report titles, MOCA database reference number, media types, analytical parameters, investigation timeline, and number of samples associated with each data source, as well as the QA/QC information that was used in the assessment process. The assigned usability category for each data source is provided in the last column of the table, as summarized below:

- **Category 1 – Data of Known Quality** – Data sets from 11 sources were assigned to this class:
  - Floodplain Sampling Event 2005 (CH2M HILL, 2005c)
  - Ecological Risk Assessment Support Sampling (CH2M HILL, 2005b)
  - Tittabawassee River Sediment Dioxin/Furan Concentration Variability (CH2M HILL, 2005a)

- March 2004 Flood Event (LTI, 2005b)
- Geochronology Pilot Study, Floodplain Soils, Tittabawassee River, Michigan (LTI, 2005a)
- 2004 Michigan State University Wildlife Sampling (MSU, 2004)
- Preliminary Analytical Results for Soil Samples taken at Residential Properties in the Tittabawassee River Floodplain by the DEQ in June through December of 2003 (MDEQ, 2004b)
- A Sediment Sampling Survey of The Saginaw River, Bay County, Michigan (MDEQ, 2004a)
- Final Report Phase II Tittabawassee/Saginaw River Dioxin Flood Plain Sampling Study (MDEQ, 2003a )
- Greenpoint-Tittabawassee River Dioxin Study Area-Phase I Sampling Study Report (MDEQ, 2001)
- Baseline Chemical Characterization of Saginaw Bay Watershed Sediments (MDEQ, 2002)
- Category 2 – Data of Partially Known Quality – Data sets from two sources were assigned to this class:
  - Analysis of Samples for the Presence of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans by High-Resolution Chromatography/High-Resolution Mass Spectrometry, August 2004 (Wilcox, 2004)
  - Suspended Solids and Bedload Transport of Nutrients, Heavy Metals, and PCBs in 16 Major Tributaries to Saginaw Bay, 1990-1992 (Jude, et al, 1993)
- Category 3 – Data of Unknown Quality – The remaining data sets were assigned to this classification due to missing or incomplete QA/QC information:
  - River Sediment Surveys Summary – Midland Area Soil and Sediment Studies and 1981 River Sediment Survey (USEPA, [1974, 1978, 1981, 1984, 1996])
  - Summary of 1996 Midland Dioxin Study Results 03/25/97, Working Draft of Document for Public Release (MDEQ, 1997)
  - Michigan Dioxin Studies – Dow Chemical Wastewater Characterization Study, Tittabawassee River Sediments and Native Fish (Amendola and Barna, 1986)

## References

- Amendola, G.A. and D.R. Barna (USEPA). 1986. Michigan Dioxin Studies, Dow Chemical Wastewater Characterization Study, Tittabawassee River Sediments and Native Fish.
- CH2M HILL. 2005a. Tittabawassee River Sediment Dioxin/Furan Concentration Variability. March.
- CH2M HILL. 2005b. Ecological Risk Assessment Support Sampling. March.
- CH2M HILL. 2005c. Transmittal of Analytical Data from Floodwater Samples. May.
- CH2M HILL. 2005d. Tittabawassee River Floodplain Scoping Study Work Plan-Revised. July.
- Jude, David J., Donna Francis, James Barresm and Scott DeBoe. 1993. Suspended Solids and Bedload Transport of Nutrients, Heavy Metals, and PCBs in 16 Major Tributaries to Saginaw Bay, 1990-1992. October.
- Limno-Tech, Inc. (LTI). 2005a. Geochronology Pilot Study Floodplain Soils, Tittabawassee River, Michigan. May.
- Limno-Tech, Inc. (LTI). 2005b. Collection and Analysis of Deposited Floodplain Sediments, March 2004. July.
- Michigan Department of Environmental Quality (MDEQ), Waste Management Division. 1997. Summary of 1996 Midland Dioxin Study Results 03/25/97, Working Draft of Document for Public Release.
- Michigan Department of Environmental Quality (MDEQ). 2001, Air Quality Division. Public Participation Documents for The Dow Chemical Company, 1261 Building, Midland, MI 48667, Permit Application Number 212-00A). July.
- Michigan Department of Environmental Quality (MDEQ). 2002. Baseline Chemical Characterization of Saginaw Bay Watershed Sediments. August.
- Michigan Department of Environmental Quality (MDEQ). 2003. Revised August 2003. Final Report Phase II Tittabawassee/Saginaw River Dioxin Flood Plain Sampling Study. June.
- Michigan Department of Environmental Quality (MDEQ). 2004a. A Sediment Sampling Survey of the Saginaw River, Bay County, Michigan.
- Michigan Department of Environmental Quality (MDEQ). 2004b. Preliminary Analytical Results for Soil Samples taken at Residential Properties in the Tittabawassee River Floodplain by the DEQ in June through December of 2003.
- Michigan State University (MSU). 2004. Wildlife Sampling.
- U.S. Environmental Protection Agency (USEPA). [1974, 1978, 1981, 1984, 1996]. Sediment Surveys.
- U.S. Environmental Protection Agency (USEPA). 1999. Contract Laboratory Program National Functional Guidelines for Organic Data Review.

U.S. Environmental Protection Agency (USEPA). 2001. Contract Laboratory Program National Functional Guidelines for Low Concentration Organic Data Review.

U.S. Environmental Protection Agency (USEPA). 2004. Contract Laboratory Program National Functional Guidelines for Inorganic Data Review.

Wilcox Professional Services (Wilcox). 2004. Analysis of Samples for the Presence of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans. August.

**TABLE A-1**  
Summary of Historical Data Quality and Usability Assessment - Tittabawassee River Area  
*Tittabawassee River and Floodplain RI Work Plan*

Study Time Frame	Author	Associated Report Name	MOCA Database Source No.	Data Source Name	Type of Media	Analytical Parameters	Sample Dates	Available QA/QC Data and/or Documents	Assigned Quality and Usability Assessment Category	Notes
2005	CH2M HILL	Transmittal of Analytical Data from Floodwater Samples	53	Floodwater Sampling Event 2005	floodplain surface water, surface water	Dioxins and furans	3/2005-4/2005	Collected under Dow QAPP and SOPs	Category 1 Data of Known Quality	
2004	MSU	Tittabawassee River Data Package (Round 1 or Preliminary Sampling	52	2004 MSU Wildlife Sampling	biota, soil, sediment, surface water	Dioxins and furans	1/2004	Laboratory reports include information about sample handling, field QA/QC and laboratory QA/QC	Category 1 Data of Known Quality	
2004	CH2M HILL	Ecological Risk Assessment Support Sampling	44	Ecological Risk Assessment	sediment, soil	Dioxins and furans General parameters Herbicides Metals Grain size PCBs Pesticides SVOCs VOCs	6/2004	Collected under Dow QAPP and SOPs	Category 1 Data of Known Quality	
2003, 2004	CH2M HILL	Tittabawassee River Sediment Dioxin/Furan Concentration Vertical Variability	42, 46	Sediment Variability, Analysis of Existing Sediment Cores	sediment	Dioxins and furans Grain size Total organic carbon	7/2004	Collected under Dow QAPP and SOPs	Category 1 Data of Known Quality	
2004	Limno-Tech, Inc	Geochronology Pilot Study, Floodplain Soils, Tittabawassee River Floodplain, Michigan	36	Geochronology Sampling - December 2004	soil	Metals Radionuclides	12/2004	Collected under Dow QAPP and SOPs	Category 1 Data of Known Quality	This report contains radionuclides data (analyzed for cesium-137 and lead-210).
2004	Limno-Tech, Inc	Collection and Analysis of Deposited Floodplain Sediments, March 2004	48	March 2004 Flood Event	soil	Dioxins and furans	3/2004	Collected under Dow QAPP and SOPs	Category 1 Data of Known Quality	
2003	MDEQ	Preliminary Analytical Results for Soil Samples taken at Residential Properties in the Tittabawassee River Floodplain by the DEQ in June through December of 2003	16	MDEQ 2003 Residential Floodplain Soil Sampling	soil	Dioxins and furans	7/2003-12/2003	This report is only 4 pages, and mostly contains summary tables of analytical results for soil samples. However other MDEQ documents from this time period suggest that the data should be equivalent in usability to MDEQ 2001 data set #159	Category 1 Data of Known Quality	
2003	MDEQ	A Sediment Sampling Survey of The Saginaw River, Bay County, Michigan	33	A Sediment Sampling Survey of The Saginaw River, Bay County, MI	sediment	PCBs	9/2003	Limited QA/QC documentation in report - However other MDEQ documents from this time period suggest that the data should be equivalent in usability to MDEQ 2001 data set #159	Category 1 Data of Known Quality	
2002	MDEQ	Final Report Phase II Tittabawassee/Saginaw River Dioxin Flood Plain Sampling Study	3	MDEQ 2002 Phase II Environmental Assessment	soil, surface water, groundwater, biota	Dioxins and furans PCBs Pesticides	5/2002-12/2002	Limited QA/QC documentation in report - However other MDEQ documents from this time period suggest that the data should be equivalent in usability to MDEQ 2001 data set #159	Category 1 Data of Known Quality	
2001	MDEQ	GreenPoint-Tittabawassee River Dioxin Study Area-Phase I Sampling Study Report	2	MDEQ 2000-2001 Phase I Environmental Assessment	soil	Dioxins and furans	12/2000-6/2001	Limited QA/QC documentation in report - However other MDEQ documents from this time period suggest that the data should be equivalent in usability to MDEQ 2001 data set #159	Category 1 Data of Known Quality	
2001	MDEQ	Baseline Chemical Characterization of Saginaw Bay Watershed Sediments	1	MDEQ 2001 Baseline	soil, sediment	Dioxins and furans Metals PCBs Pesticides SVOCs VOCs	8/2001-12/2001	The planning document (Sampling and Analysis Plan, attached as Appendix 3) provides information on COC and sample tracking procedures (although no COC documents are attached in the final report). The associated report and the planning document (Sampling and Analysis Plan, attached as Appendix 3) contain discussions on analytical procedures/methods, and detection limits. The associated report and the planning document (Sampling and Analysis Plan, attached as Appendix 3) contain discussions on sample holding times, temperature criteria, preservation methods, and/or sample preparation. QC data (solvent blank, duplicate method blank, duplicate matrix spike, trip blanks) are available to assess accuracy and precision. Laboratory data qualifier flags (not data quality assurance review flags) are also available.	Category 1 Data of Known Quality	
2004	Wilcox Professional Services	Analysis of Samples for the Presence of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans by High-Resolution Chromatography/High-Resolution Mass Spectrometry, August 2004	45	Analysis of Samples for the Presence of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans, August 2004	soil	Dioxins and furans	6/2004	This document was prepared by Eno River Labs, LLC as a laboratory analytical results report. The document is 828 pages long, and mostly consists of raw lab data sheets.	Category 2 Data of Partially Known Quality	
1992	University of Michigan, Center for Great Lakes (Jude et. al)	Suspended Solids and Bedload Transport of Nutrients, Heavy Metals, and PCBs in 16 Major Tributaries to Saginaw Bay, 1990-1992	9	U. Mich. 1990-92 Saginaw River and Tributaries Water and Bedload Survey	sediment, surface water	Metals PCBs	9/1990-7/1992	No information is available on sample traceability (no COC or other type of sample tracking information). The associated report contains information on analytical procedures/methods; detection limits are not reported with the raw data; parameter values below the limit of detection are assigned a value of zero. The associated report contains some information on sample holding times, temperature criteria, preservation methods, and/or sample collection or preparation in the field. Limited QC data (replicate analyses of same sample) are available to assess accuracy and precision.	Category 2 Data of Partially Known Quality	
1996	MDEQ	River Sediment Surveys Summary - Midland Area Soil and Sediment Studies	11	1996 MDEQ Tittabawassee River Sediment Survey	sediment	Dioxins and furans	9/1996	Abstract only - original document is not available.	Category 3 Data of Unknown Quality	

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Study Time Frame	Author	Associated Report Name	MOCA Database Source No.	Data Source Name	Type of Media	Analytical Parameters	Sample Dates	Available QA/QC Data and/or Documents	Assigned Quality and Usability Assessment Category	Notes
1996	MDEQ	Summary of 1996 Midland Dioxin Study Results 03/25/97, Working Draft of Document for Public Release (Mar. 1997)	14	MDEQ Summary of 1996 Midland Dioxin Study Results	soil	Dioxins and furans	9/1996	No information is available on sample traceability, analytical procedures/methods, detection limits, or QC sample data.	Category 3 Data of Unknown Quality	
1985	USEPA Region V (Amendola, G.A. and D.R. Barna)	Michigan Dioxin Studies - Dow Chemical Wastewater Characterization Study, Tittabawassee River Sediments and Native Fish (Jul. 1986)	4	EPA 1986 Michigan Dioxin Studies (1978, 1981, 1984 Sediment and Fish Assessment, Gary Amendola)	biota, sediment, surface water, soil	Dioxins and furans PCBs Pesticides	6/1978-10/1985	No information is available on sample traceability, analytical procedures/methods, detection limits, or QC sample data.	Category 3 Data of Unknown Quality	
1981	USEPA GLNPO (Amendola, G.A. and D.R. Barna)	River Sediment Surveys Summary - 1981 River Sediment Survey	8	USEPA 1983 Tittabawassee River Sediment Survey	sediment	Metals PCBs Pesticides	6/1981	No information is available on sample traceability, analytical procedures/methods, detection limits, or QC sample data.	Category 3 Data of Unknown Quality	Abstract only - original document is not available.

**NOTES:**  
PCB = Polychlorinated Biphneyls  
SVOC = Semivolatiles  
VOC = Volatiles